Friction **4**(4): 303–312 (2016)
DOI 10.1007/s40544-016-0117-7
ISSN 2223-7690
CN 10-1237/TH
RESEARCH ARTICLE

Investigation of the mechanisms for stable superlubricity of poly(vinylphosphonic acid) (PVPA) coatings affected by lubricant

Caixia ZHANG[1], Zhifeng LIU[1], Yuhong LIU[2,*], Qiang CHENG[1], Congbin YANG[1], Ligang CAI[1]

[1] *Beijing Key Laboratory of Advanced Manufacturing Technology, Beijing University of Technology, Beijing 100124, China*

[2] *State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China*

Received: 16 April 2016 / Revised: 19 May 2016 / Accepted: 20 June 2016

Abstract: The stability of the tribological properties of polymer coatings is vital to ensure their long term use. The superlubricity of the poly(vinylphosphonic acid) (PVPA)-modified Ti6Al4V/polytetrafluoroethylene (PTFE) interface can be obtained when lubricated by phosphate-buffered saline (PBS, pH = 7.2), but not when lubricated by deionized water and ethanol. Therefore, the mechanisms for the superlubricity of PVPA coatings affected by lubricant were investigated in detail. The stability of the PVPA coatings and their compatibility with the lubricant are critical factors in realizing ideal tribological properties of PVPA coatings. Robust PVPA coatings are stable under a wide range of pH values (6–10) using PBS as the basic solution, and are also characterized by superlubricity. The hydrolysis kinetics of phosphate anhydride is the main reason for the pH responses. In addition, along with stability, PVPA coatings exhibit different friction coefficients in salt solutions which are composed of various ions, which indicates that the compatibility between PVPA coatings and the lubricant can be used to regulate the superlubricity properties. Based on a fundamental understanding of the mechanism of surperlubricity by considering the effects of the lubricant, PVPA coatings with stability and perfect tribological performance are expected to be applied in more aspects.

Keywords: superlubricity; poly(vinylphosphonic acid); stability; compatibility with lubricant

1 Introduction

Friction and lubrication failure are the primary reasons for the poor stability of cervical disc replacements [1]. Surface characteristics seriously influence their performance in the human body. As such, improving the stability and service life of artificial cervical discs via surface modification is receiving increased attention [2–6]. Inspired by some biological synovial joints, such as knees, hips, and shoulders, which display excellent tribological properties from the support of water-based lubricants due to the highly hydrated macromolecular polymers attached to their surfaces [7, 8], many research groups paid sufficient attention in surface modifications with hydrophilic polymers. The tethering of hydrophilic polymers on surfaces has been widely reported as being associated with superlow friction properties in aqueous solutions. Poly(ethylene glycol) (PEG) has been widely studied as an effective polymer for achieving ultralow friction [9]. Cross-linked chitosan and hyaluronan layers can be resistant to wear and protein adsorption [10]. pMPC-modified surfaces showed a low friction coefficient below 0.01, due to the highly hydrated phosphorylcholine-like monomers on 2-methacryloxyethyl phosphorylcholine (pMPC) chains [11–13].

Despite the excellent frictional properties of hydrophilic polymer-modified surfaces, the stability of their tribology is of more critical importance due to the implants being located adjacent to neural structures. Therefore, the robustness of dramatic tribological responses was successively investigated in

* Corresponding author: Yuhong LIU.
E-mail: liuyuhong@tsinghua.edu.cn

numerous studies. Lubricants can affect the tribological properties. Precise investigations have found that solvent quality influences the stability of polymer brushes [14, 15]. When polymer-modified surfaces slide in "good" solvents, friction can be greatly reduced due to the maximum swell of the polymer chains. However, polymer brushes will collapse due to minimal contact between the polymer chains and the solvent in a "poor" solvent, which leads to a significant increase in friction [16, 17]. pH is a basic characteristic of lubricants, whose change will influence the characteristics of polymer. The pH-dependent protonation of amine groups and conformational rearrangements of poly(N,N-dimethylaminoethyl methacrylate) brushes in alkaline, neutral, and acidic solutions leads to different swelling and deswelling rates [18]. Further, the tribological properties of polymer-modified surfaces have been proved to be affected by pH, especially for hydrophobic polymer [19].

In addition, according to research by Zhou, the swelling and collapse of polymer brushes caused by the constituents of lubricants also greatly influence their lubricating capabilities [20]. That is, the compatibility between the surface properties of tribo-pairs and the lubricant is critical in superlubricity. The interfaces of silicon-nitride/water [21] and phosphoric acid/quartz [22, 23] displayed superlubricity with the help of a lubricant by a tribochemical reaction with the tribo-pairs. High-density poly(methyl methacrylate) (PMMA) brushes showed low friction coefficient in response to toluene, due to the moderate interaction between the brush surface and the sliding probe, whereas the opposite phenomenon occurs in hexane [24]. MPC was widely researched in surface modification used in artificial joints. However, the lubricity of MPC is reduced in toluene, probably due to more collapsed MPC brushes and decreased solvent uptake in the coating [25]. For the same reasons, MPC do not exhibit good tribological properties in ethanol and water mixtures [26]. In addition, with respect to polyelectrolytes, the compatibility of the charging characteristics between the ions in lubricants and polymer brushes is also a critical factor for reducing the friction coefficient, due to the influences of electrostatic and hydrophobic interactions [27].

In this study, the tribological performances of poly(vinylphosphonic acid) (PVPA) coatings in different lubricants were explored on a ball-on-disc machine. Our experimental results showed that ultralow friction and wear of PVPA-modified Ti6Al4V could be achieved over a wide pH range. However, even with stability, PVPA coatings showed different friction coefficients in various salt solutions, indicating that the compatibility between PVPA coatings and lubricants regulates the superlubricity properties. PVPA-modified Ti6Al4V displayed excellent tribological properties in a great number of lubricants, which thus extends their applications.

2 Materials and methods

2.1 Materials

PVPA (97%) with the average molecular weight of 24,817 g/mol and phosphate-buffered saline (PBS, pH = 7.2) were purchased from Sigma Aldrich. All inorganic salts were purchased from Sinopharm. The lubricants, unless otherwise specified, were prepared by adding appropriate inorganic salts into deionized water to obtain salt solvents (pH = 7.2). Ti6Al4V (50 mm × 50 mm, 1 mm thickness) foils were supplied by Goodfellow, Inc. To achieve smooth surfaces (Ra ≈ 2 nm), these foils were then cut and polished. Polytetrafluoroethylene (PTFE) balls (D ≈ 6 mm, Ra ≈ 280 nm) were obtained from Quanying, Inc. All reagents mentioned above were used without purification.

2.2 Universal micro-tribometer for the evaluation of tribological properties

Formation details and mechanism of the PVPA coating on Ti6Al4V were discussed in our last paper [28]. The tribological performance of PVPA-modified Ti6Al4V in different lubricants was investigated on a machine called universal micro-tribometer (UMT-3, CETR). PTFE balls were chosen as another tribo-pair during reciprocating movement. In all measurements, temperature was controlled at 37 °C. The normal load was chosen as 2.5 N, which yielded a nominal contact pressure of 25.19 MPa in our experiments, while the average sliding speed used was 12 mm/s. All tribological experiments were carried out in a lubricating system of complete immersion. The same friction coefficient during back and forth movements can be sustained by carefully regulating the down-holder.

2.3 X-ray photoelectron spectroscopy (XPS) for detecting elements of the PVPA coatings on Ti6Al4V

The surface composition of PVPA-modified Ti6Al4V in the wear tracks were characterized by XPS. These measurements were carried out on an ESCALAB 250 XI (Thermo Scientific Instrument, USA) equipped with a monochromatized Al K R X-ray source. All spectra were obtained at a 90° photoelectron takeoff angle from the surface. Two spots on two replicates of each sample were analyzed. The data for each element represent averages of the peak intensities determined at each spot. All binding energy values were charge-referenced to the C1s peak at 285 eV. Data analysis was performed with software (Thermo Advantage v5.41) to calculate the elemental and component composition from the peak areas.

2.4 Contact angle goniometry

The wetting abilities of PVPA-modified Ti6Al4V with different lubricants were investigated in terms of contact angle. Contact angles were measured using a JC2000A (POWEREACH, Inc.) system. A drop with the volume of 2 μL was placed on each test point to measure static contact angles. Three spots of each sample were examined. The values were obtained by averaging values of nine spots on three samples.

2.5 Stereo light microscope for evaluating the wear on the two tribo-pairs

A stereo light microscope (SZX12, OLYMPUS, Japan) was used to test the scratches on the Ti6Al4V and the wear scars on the PTFE balls following the experiments. The test areas were amplified at least 10-fold to clearly display the morphology. At least three repetitions of each experiment were performed.

3 Results and discussion

3.1 Tribological performance of PVPA coatings in different lubricants

PVPA coatings precisely control the surface chemistry of Ti6Al4V. To explore the effect of lubricants on PVPA coatings, tribological behaviors of PVPA-modified Ti6Al4V were evaluated in different lubricants. Figure 1(a) shows a summary of the friction coefficient results. When the entire system was immersed in PBS (pH = 7.2), the friction coefficient of PVPA-modified Ti6Al4V sliding against PTFE balls was ultralow (approximately 0.005) at an average sliding speed of 12 mm/s, with a normal load of 2.5 N, yielding an initial contact pressure of 25.19 MPa. A superlow and stable friction coefficient is the common state of natural joints and is the desired outcome for artificial joints. However, when lubricated by water and ethanol, the friction coefficient of the PVPA-modified Ti6Al4V/PTFE interface shows a dramatic increase compared to the result for PBS, approximately 0.02 for ethanol and 0.03 for water. Reasons for the difference on friction coefficient were firstly investigated by analyzing wear track. Figure 1(b) displays the XPS spectra collected

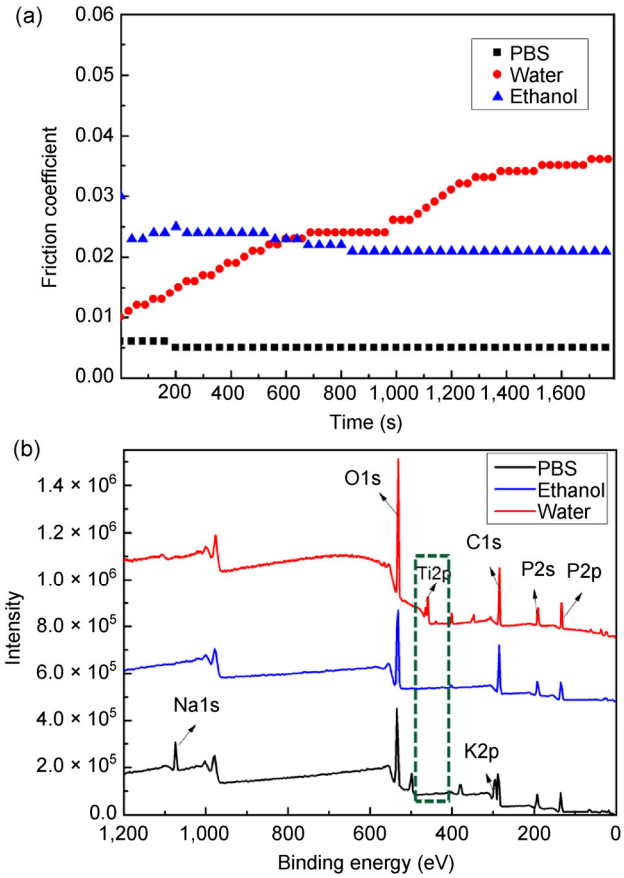

Fig. 1 Tribological properties of PVPA-modified Ti6Al4V lubricated by PBS, water, and ethanol: (a) variations in the friction coefficient of PVPA-modified Ti6Al4V sliding against PTFE balls, and (b) XPS survey scans of the wear track on PVPA-modified Ti6Al4V after sliding for 0.5 h.

from the wear tracks after tribological experiments in different lubricants. In contrast to the other results, Ti2p peak can be found in the sample lubricated by water. Therefore, the PVPA coatings were damaged when tribological experiments were performed in water, which explains the increased friction coefficient. However, a very interesting thing can be found by carefully analyzing the spectrum (the blue line in Fig. 1(b)) collected from the wear trace of the PVPA-modified Ti6Al4V lubricated by ethanol. The P2s and P2p peaks are high, but no Ti2p peak can be found, which is similar to the results of the PVPA-modified Ti6Al4V lubricated by PBS, but with a high friction coefficient.

A comprehensive analysis of the tribological results of PVPA-modified Ti6Al4V in water and PBS confirms that the basic condition for ensuring the superlubricity of PVPA coatings is their stability in lubricants. In addition, the experimental results that lubricated by PBS and ethanol ensure that stability is not the only reason for the superlubricity. While PVPA coatings are robust in ethanol, superlubricity is not achieved due to the differences in the tribological interface properties. There are several reasons. The PVPA molecules used in our research contain a large number of phosphate groups, whose hydrophilic performance is remarkable, and show excellent properties in reducing friction [22]. It is assumed that hydration sheaths may be formed around the PVPA molecular chains that stretch outward from the surface of the PVPA coatings. Water molecules trapped in these hydration sheaths are exchanged quickly with other hydration or free water molecules [11, 28], which maintain a fluid-like manner at the interface, and thus increase the lubricity in the contact region. In addition, water molecules will adsorb onto salt ions in PBS, forming a sort of molecular ball bearing, which also improves the boundary lubrication.

In addition, compatibility between the tribo-pairs and lubricants is critical in achieving superlubricity. Figure 2 shows the measurement results of contact angle on PTFE. Owing to the abundant fluoride within PTFE, PTFE presents super hydrophobic nature. The contact angle of water on the PTFE surface is approximately 130°, as shown in Fig. 2(a). Therefore, with the adsorbed water molecules on PVPA coatings,

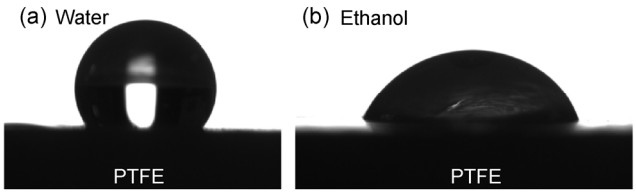

Fig. 2 Contact angle on PTFE: (a) water and (b) ethanol.

there is little adhesive force between two tribo-pairs, which can further reduce the shearing resistance and lead to a superlow friction coefficient. However, the contact angle of ethanol is only about 70° (Fig. 2(b)), associated with a larger adhesive force, which increases the friction.

According to the analysis above, the superlubricity of PVPA-modified Ti6Al4V is related to its stability and compatibility with lubricants. Therefore, designs must simultaneously consider the robustness of polymer coatings and lubricant compatibility to improve the tribological properties.

3.2 Novel pH-stable frictional behaviors and mechanisms of PVPA-modified Ti6Al4V in PBS

The stability of PVPA coatings provides basic assurance for the superlubricity of PVPA-modified Ti6Al4V. The robustness of PVPA coatings on Ti6Al4V has been proved in neutral PBS. To further investigate the mechanism for the stability of coatings and to expand the application of PVPA-modified Ti6Al4V, their tribological properties were evaluated in PBS, whose pH are regulated to 5, 6, 7.2, 8, 9, 10, 11 and 12 using sodium hydroxide and hydrochloric acid successively. Friction tests were performed without changing other experimental parameters. Figure 3(a) shows the average friction coefficients versus pH. When pH is in the range of 6 to 11, the friction coefficient is approximately 0.005, which proves the negligible effects of pH on superlubricity. Further, the curves of the friction coefficients versus time for pH variation from 6 to 11 in Fig. 3(b) display only small fluctuations in each curve, confirming the excellent stability of PVPA coatings over a wide pH range.

However, when PVPA-modified Ti6Al4V was immersed into acidic conditions (pH = 5), the friction coefficient increased to about 0.009. The reasons for this can be determined from the wear morphology of

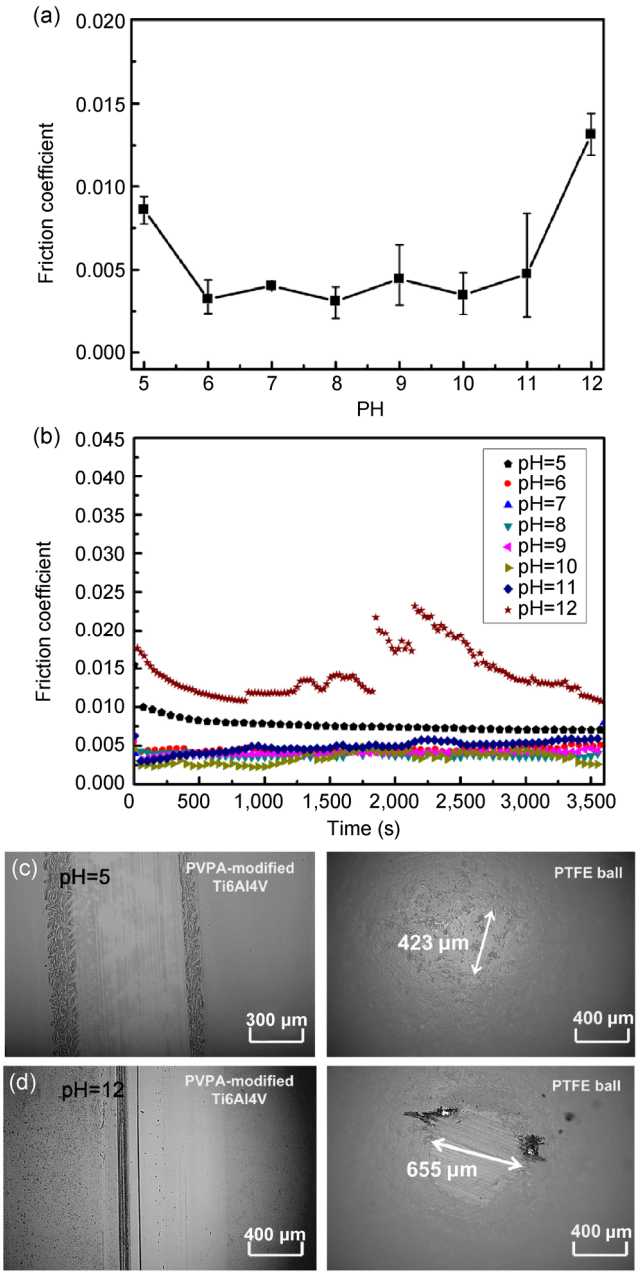

Fig. 3 Tribological properties of PVPA-modified Ti6Al4V lubricated by PBS with different pH values: (a) average friction coefficients versus pH, (b) curves of friction coefficients versus time for pH values in the range of 5 to 12, (c) wear patterns at a pH of 5, and (d) wear patterns at a pH of 12.

the two tribo-pairs after sliding for 2 h, as shown in Fig. 3(c). The PVPA coatings on modified Ti6Al4V collapse and are worn through when sliding against PTFE in PBS (pH = 5), indicating their weak stability. Fortunately, the PVPA coatings are not completely collapsed, which can be ensured by the stacked coating on the edge of the scratches. Therefore, wear on the PTFE ball is not severe, showing a wear scar of 423 μm. This result indicates that PVPA coatings can only maintain stability in weak-acid lubricants. The superlubricity of PVPA-modified Ti6Al4V will disappear when the pH is below 6. Moreover, in the case of pH = 12, the friction coefficient is especially high with huge fluctuations, as shown in the star point curve in Fig. 3(b). In these conditions, the PVPA coatings were destroyed completely. The left picture in Fig. 3(d) displays the wear trace on PVPA-modified Ti6Al4V. Apart from the distinct scratch, no PVPA coatings can be found. In accordance with the collapse of the PVPA coatings, a large wear scar with a diameter of 655 μm appears on the PTFE ball. This phenomenon makes it clear that PVPA coatings are only robust in alkaline lubricants whose pH is below 12.

From the above analysis, it is assumed that the superlubricity of PVPA-modified Ti6Al4V can be obtained not only in a neutral lubricant, but also in weak-acid and weak-base lubricants. Moreover, the stability of PVPA coatings is more sensitive to acid. In weak-acid and weak-base lubricants, the collapse of PVPA coatings is the main reason for the absence of superlubricity. Therefore, the mechanisms for stability of PVPA coatings in lubricants were analyzed. The PVPA coatings are linked to titanium alloy through Ti–O–P due to the chelating properties of phosphate groups to titanium, which has been well confirmed [29, 30]. These covalent links ensure the stability of the underlying PVPA molecular layer. Further, within the coatings, interchain condensation [31] between two phosphonic acid groups forms phosphonic acid anhydrides, which accounts for the cross-link between the PVPA molecules in the coatings [28]. Unfortunately, phosphate anhydrides, whose stability is sensitive to water molecules [32, 33], will be hydrolyzed in some water-based solvents. The anhydride hydrolysis reaction begins with the attack of a hydrogen or hydroxyl ion. If phosphate anhydrides are in acid condition, the hydrogen ion is the inducing factor for the hydrolysis reaction, as shown in Expression (1). With the hydrolysis of anhydrides, free PVPA molecules and then the phosphate groups in the lubricant will constantly increase. More hydrogen ions are then ionized, which accelerates the

hydrolysis reaction. When the PBS buffer function is ineffective, the pH of the lubricant will continue to decrease, leading to the collapse of the PVPA coatings. Similarly, if the phosphate anhydrides are in alkaline conditions, the hydroxyl ion is the critical factor. Expression (2) shows the hydrolysis reaction of phosphate anhydrides in an alkaline environment. With the increased number of free PVPA molecules from the hydrolysis of anhydrides, the number of hydrogen ions will increase, leading to a neutral reaction between the hydrogen and hydroxyl ions, which will be in favor of decreasing pH value and maintaining the stability of the anhydrides. This phenomenon explains the wider pH range in which PVPA coatings are stable under alkaline rather than acid environments. Obviously, the higher the pH value, the more the PVPA coatings will be destroyed before the pH of the lubricant becomes neutral. Therefore, the superlubricity of PVPA coatings can be maintained within a pH range of 6 to 11, which is consistent with their stability.

$$RPO_2H\text{-}O\text{-}PO_2HR + H_2O = 2RPO_3H_2 \quad (1)$$

$$RPO_2H\text{-}O\text{-}PO_2HR + 2OH^- = 2RPO_3H^- + H_2O \quad (2)$$

3.3 Superlubricity of PVPA-modified Ti6Al4V regulated by the compatibility with lubricants

PVPA coatings with perfect stability in PBS display ultralow friction. In order to extend the range of their application, as required in artificial joint replacements, the mechanism of compatibility between PVPA coatings and lubricants was investigated. Considering the buffer function of PBS, the lubricants were simplified to salt solutions with buffer ions. Water-based lubricants with Na_2HPO_4, $(NH_4)_3PO_4$ and $NaHCO_3$ were prepared respectively. The salt ion concentration in all lubricants was 0.05 M, which is the same as that of PBS. pH of the three lubricants was regulated to 7.2 according to their identity using sodium hydroxide and hydrochloric acid. Then, The PVPA-modified Ti6Al4V disks were lubricated with the above solutions and tested them against a 6.35-mm PTFE ball at a sliding speed of 12 mm/s under an initial pressure of 25.19 MPa. The contact pressures are large enough to ensure that the artificial cervical discs are used at a safe level for the human body. The friction coefficients of PVPA-modified Ti6Al4V in these salt solvents are all less than 0.01 with very little fluctuation, as shown in Fig. 4(a), thus indicating their superlubricity. In addition, Figs. 4(b), 4(c), and 4(d) show the surface topographies of two tribo-pairs after sliding successively for 0.5 h. The absence of wear tracks strongly confirms the ultralow wear. The experimental data show that PVPA coatings can be stable in buffer salt ion solutions other than PBS, further accompanied with the result of superlubricity. That is, the superlubricity property

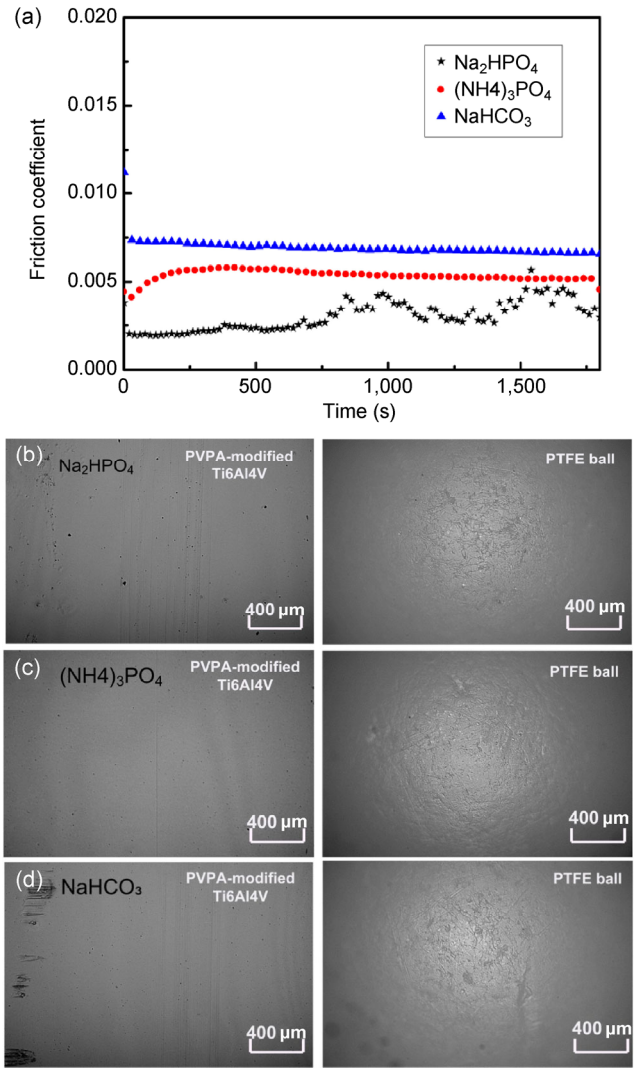

Fig. 4 Tribological properties of PVPA-modified Ti6Al4V in different lubricants: (a) average friction coefficients versus time, (b) surface topography on two tribo-pairs after sliding for 0.5 h in Na_2HPO_4, (c) surface topography on two tribo-pairs after sliding for 0.5 h in $(NH_4)_3PO_4$, and (d) surface topography on two tribo-pairs after sliding for 0.5 h in $NaHCO_3$.

of PVPA coatings can be generalized to other salt solutions with a buffer function, which will extend the range of their application. The reason may be that the salt ions help to stabilize the PVPA coatings, so the hydrolysis reaction of the phosphate anhydrides is slow. Also, even with few hydrogen ions produced by hydrolysis, salt ions with a buffer function can regulate a lubricant to be neutral and thus ensure stability of the PVPA coatings and further the superlubricity.

However, a careful analysis of Fig. 4(a) reveals that the friction coefficient of PVPA coatings lubricated by $NaHCO_3$ solution is larger than those of $(NH_4)_3PO_4$ and Na_2HPO_4. This phenomenon is associated with the interfacial properties in the contact area. The properties of the phosphate groups in $(NH_4)_3PO_4$ and Na_2HPO_4 are similar to that in PVPA molecular chains. Therefore, their influence on the interfacial properties is negligible. However, HCO_3^- in $NaHCO_3$ solution may disturb the lubricating property of phosphate groups on PVPA molecules at the frictional interface by changing their hydrophilic characteristics, leading to the increased friction coefficient. Therefore, it is assumed that the compatibility between PVPA coatings and lubricants is another factor influencing superlubricity, since PVPA coatings have been shown to be robust in those lubricants.

With a fundamental understanding of the mechanism responsible for the superlubricity of PVPA coatings, tribological properties of PVPA coatings were researched in more variety of lubricants. Inspired by the experimental results for pH in the range of 6 to 11, the conclusion that the superlubricity of PVPA coatings is independent with pH can be obtained. Therefore, the lubricants were simplified to salt solutions without any buffer function further. NaCl, $NaNO_3$, and Na_2SO_4 solutions of 0.05 M were regulated. Friction tests were performed using these solutions as lubricants without changing other experimental parameters. The friction coefficients in Fig. 5(a) are all less than 0.01 without running-in time. There is very little fluctuation of the curves, indicating the stability of the superlubricity property. In addition, ignorable wear on the surfaces of two tribo-pairs (Figs. 5(b), 5(c), and 5(d)) indicates anti-wear properties and the stability of the PVPA coatings lubricated by these lubricants. Based on the above analysis, the

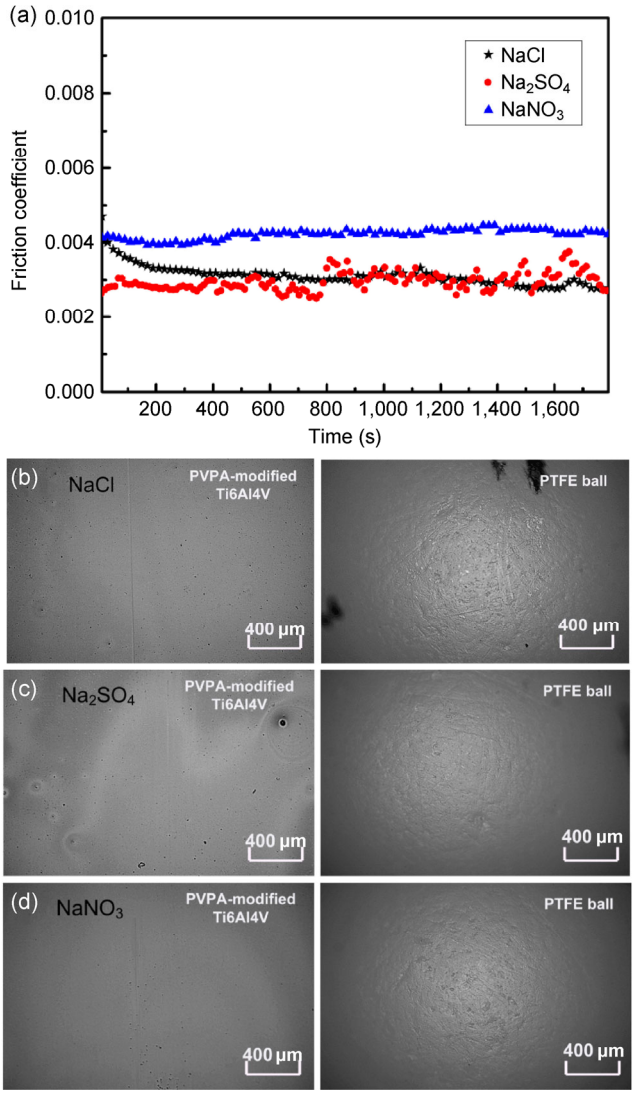

Fig. 5 Tribological properties of PVPA-modified Ti6Al4V in different lubricants: (a) average friction coefficients versus time, (b) surface topography on two tribo-pairs after sliding for 0.5 h in NaCl, (c) surface topography on two tribo-pairs after sliding for 0.5 h in Na_2SO_4, and (d) surface topography on two tribo-pairs after sliding for 0.5 h in $NaNO_3$.

ideal tribological properties of PVPA coatings can be extended to a wider variety of salt solutions, which lack buffer functions. There are several reasons that salt ions without any buffer function help maintain superlubricity. One reason can be revealed by comparing the XPS results in Fig. 1(b) with the surface topography of PVPA-modified Ti6Al4V in Figs. 5(b), 5(c), and 5(d), which show that salt ions can help improve the stability of PVPA coatings to maintain their surperlubricity. In addition, according to Klein's research [34], water

molecules adsorbing on salt ions retain the shear fluidity characteristics of the bulk liquid, which may further account for the lower friction coefficient compared to that of water.

4 Conclusions

The stable superlubricity of the poly(vinylphosphonic acid) (PVPA)-modified Ti6Al4V/polytetrafluoroethylene (PTFE) interface is regulated by lubricants. Phosphate-buffered saline (PBS, pH = 7.2) is a "good" lubricant for PVPA coatings, but deionized water and ethanol are not. The robustness of PVPA coatings is the main reason for their ideal tribological properties. PVPA coatings are stable in lubricants regulated based on PBS, whose pH ranges widely from 6 to 11, as well as being characterized by superlubricity. The hydrolysis kinetics of phosphate anhydride is responsible for the pH-response result. Further, compatibility with the lubricant is a critical factor in the surperlubricity of PVPA coatings. The friction coefficient of PVPA coatings lubricated by the $NaHCO_3$ solution is larger than those of $(NH_4)_3PO_4$ and Na_2HPO_4, due to the influence of ions on the frictional interface. Anions with stronger hydration are more beneficial in reducing the friction coefficient. In addition, with stability, PVPA coatings perform superlubricity in a variety of salt solutions without buffer functions. With a fundamental understanding of the synergistic mechanism between PVPA coatings and lubricants, the superlubricity of PVPA coatings is expected to be a wide application.

Acknowledgements

We are grateful to Guoshun Pan, associate professor of Tsinghua University, for kindly providing the polishing solution of titanium for us. The authors also appreciate the funding supported by the Beijing Natural Science Foundation (No. 3164040) and the Tribology Science Fund of State Key Laboratory of Tribology (No. STLEKF15A01), as well as the National Natural Science Foundation of China (Nos. 51522504, 51575009, and 51575010).

References

[1] Veruva S Y, Steinbeck M J, Toth J, Alexander D D, Kurtz S M.. Which design and biomaterial factors affect clinical wear performance of total disc replacements? A systematic review. *Clin Orthop Relat Res* **472**: 3759–3769 (2014)

[2] Muir BVO, Myung D, Knoll W, Frank C W. Grafting of cross-linked hydrogel networks to titanium surfaces. *ACS Appl Mater Interfaces* **6**: 958–966 (2014)

[3] Wang K, Xiong D S, Niu Y. Novel lubricated surface of titanium alloy based on porous structure and hydrophilic polymer brushes. *Appl Surf Sci* **317**: 875–883 (2014)

[4] Wu H, Zhang X, He X, Li M, Huang X, Hang R, Tang B.Wear and corrosion resistance of anti-bacterial Ti-Cu-N coatings on titanium implants. *Appl Surf Sci* **317**: 614–621 (2014)

[5] Luo Y, Chai W, Yang L, Tian M, Xu H, Chen W. The surface characterization of microporous titanium carbide coating on titanium alloys. *Proc IMechE, Part J: J Eng Tribol* **228**: 521–528 (2014)

[6] Wang S, Liao Z, Liu Y, Liu W. Different tribological behaviors of titanium alloys modified by thermal oxidation and spraying diamond like carbon. *Surf Coats Technol* **252**: 64–73 (2014)

[7] Seror J, Merkher Y, Kampf N, Collinson L, Day A J, Maroudas A, Klein J. Articular cartilage proteoglycans as boundary lubricants: structure and frictional interaction of surface-attached hyaluronan and hyaluronan-aggrecan complexes. *Biomacromolecules* **12**: 3432–3443 (2011)

[8] Murakami T, Yarimitsu S, Nakashima K, Sawae Y, Sakai N. Influence of synovia constituents on tribological behaviors of articular cartilage. *Friction* **2**: 150–162 (2013)

[9] Lee S, Zürcher S, Dorcier A, Luengo G S, Spencer N D. Adsorption and Lubricating properties of poly(L-lysine)-graft-poly(ethylene glycol) on human-hair surfaces. *ACS Appl Mater Interfaces* **1**: 1938–1945 (2009)

[10] Bongaerts J H H, Cooper-White J J, Stokes J R. Low biofouling chitosan-hyaluronic acid multilayers with ultra-low friction coefficients. *Biomacromolecules* **10**: 1287–1294 (2009)

[11] Chen M, Briscoe W H, Armes S P, Klein J. Lubrication at physiological pressures by polyzwitterionic brushes. *Science* **323**: 1698–1701 (2009)

[12] Kyomoto M, Moro T, Saiga K, Miyaji F, Kawaguchi H, Takatori Y, Nakamura K, Ishihara K.. Lubricity and stability of poly(2-methacryloyloxyethyl phosphorylcholine) polymer layer on Co-Cr-Mo surface for hemi-arthroplasty to prevent degeneration of articular cartilage. *Biomaterials* **31**: 658–668 (2010)

[13] Zhao Y, Tu Q, Wang J, Huang N. Crystalline TiO_2 grafted with poly(2-methacryloyloxyethyl phosphorylcholine) via surface-initiated atom-transfer radical polymerization. *Appl Surf Sci* **257**: 1596–1601 (2010)

[14] Ross R S, Pincus P. The polyelectrolyte brush–Poor solvent. *Macromolecules* **25**: 2177–2183 (1992)

[15] Pryamitsyn V A, Leermakers F A M, Fleer G J, Zhulina E B. Theory of the collapse of the polyelectrolyte brush. *Macromolecules* **29**: 8260–8270 (1996)

[16] Chen J, Hsieh C-Y, Huang C-F, Li P-M, Kuo S-W, Chang F-C. Using solvent immersion to fabricate variably patterned poly(methyl methacrylate) brushes on silicon surfaces. *Macromolecules* **41**: 8729–8736 (2008)

[17] Limpoco F T, Advincula R C, Perry S S. Solvent dependent friction force response of polystyrene brushes prepared by surface initiated polymerization. *Langmuir* **23**: 12196–12201 (2007)

[18] Thomas M, Gajda M, Naini C A, Franzka S, Ulbricht M, Hartmann N. Poly(N,N-dimethylaminoethyl methacrylate) brushes: pH-dependent switching kinetics of a surface-grafted thermoresponsive polyelectrolyte. *Langmuir* **31**: 13426–13432 (2015)

[19] Willott J D, Humphreys B A, Murdoch T J, Edmondson S, Webber G B, Wanless E J. Hydrophobic effects within the dynamic pH-response of polybasic tertiary amine methacrylate brushes. *Phys Chem Chem Phys* **17**: 3880–3890 (2015)

[20] Wei Q, Cai M, Zhou F, Liu W. Dramatically tuning friction using responsive polyelectrolyte brushes. *Macromolecules* **46**: 9368–9379 (2013)

[21] Xu J G, Kato K. Formation of tribochemical layer of ceramics sliding in water and its role for low friction. *Wear* **245**: 61–75 (2000)

[22] Li J J, Zhang C H, Luo J B. Superlubricity behavior with phosphoric acid-water network induced by rubbing. *Langmuir* **27**: 9413–9417 (2011)

[23] Sun L, Zhang C H, Li J J, Liu Y H, Luo J B. Superlubricity of Si_3N_4 sliding against SiO_2 under linear contact conditions in phosphoric acid solutions. *Science China-Technological Sciences* **56**: 1678–1684 (2013)

[24] Sakata H, Kobayashi M, Otsuka H, Takahara A. Tribological properties of poly(methyl methacrylate) brushes prepared by surface-initiated atom transfer radical polymerization. *Polymer J* **37**: 767–775 (2005)

[25] Kobayashi M, Terayama Y, Hosaka N, Kaido M, Suzuki A, Yamad N, Torikai N, Ishihara K, Takahara A. Friction behavior of high-density poly(2-methacryloyloxyethyl phosphorylcholine) brush in aqueous media. *Soft Matter* **3**: 740–746 (2007)

[26] Kiritoshi Y, Ishihara K. Preparation of cross-linked biocompatible poly(2-methacryloyloxyethyl phosphorylcholine) gel and its strange swelling behavior in water/ethanol mixture. *Journal of Biomaterials Science-Polymer Edition* **13**: 213–224 (2002)

[27] Zhang R, Ma S, Wei Q, Ye Q, Yu B, van der Gucht J, Zhou F. The weak interaction of surfactants with polymer brushes and its impact on lubricating behavior. *Macromolecules* **48**: 6186–6196 (2015)

[28] Zhang C X, Liu Y, Wen S, Wang S. Poly(vinylphosphonic acid) (PVPA) on titanium alloy acting as effective cartilage-like superlubricity coatings. *ACS Appl Mater Interfaces* **6**: 17571–17578 (2014)

[29] Gawalt E S, Avaltroni M J, Koch N, Schwartz J. Self-assembly and bonding of alkanephosphonic acids on the native oxide surface of titanium. *Langmuir* **17**: 5736–5738 (2001)

[30] Petrovic Z, Katić J, Metikoš-Huković M, Dadafarin H, Omanovic S. Modification of a nitinol surface by phosphonate self-assembled monolayers. *J Electrochem Soc* **158**: F159–F165 (2011)

[31] Lee Y J, Bingöl B, Murakhtina T, Sebastiani D, Meyer W H, Wegner G, Spiess H W. High-resolution solid-state NMR studies of poly(vinyl phosphonic acid) proton-conducting polymer: Molecular structure and proton dynamics. *J Phys Chem B* **111**: 9711–9721 (2007)

[32] Kaltbeitzel A, Schauff S, Steininger H, Bingöl B, Brunklaus G, Meyer W H, Spiess H W. Water sorption of poly(vinylphosphonic acid) and its influence on proton conductivity. *Solid State Ionics* **178**: 469–474 (2007)

[33] Jiang F, Kaltbeitzel A, Zhang J, Meyer W H. Nano-spheres stabilized poly(vinyl phosphonic acid) as proton conducting membranes for PEMFCs. *International Journal of Hydrogen Energy* **39**: 11157–11164 (2014)

[34] Raviv U, Klein J. Fluidity of bound hydration layers. *Science* **297**: 1540–1543 (2002)

Caixia ZHANG. She received her Ph.D. degree in mechanical engineering in 2015 from Tsinghua University, Beijing, China. After then, she joined Beijing Key Laboratory of Advanced Manufacturing Technology, Beijing University of Technology. Her research interests include biotribology, superlubricity, surface and interface analysis.

Yuhong LIU. She received her Ph. D. degree in CAS Key Laboratory of Molecular Nanostructure & Nanotechnology Institute of Chemistry, Chinese Academy of Sciences, Beijing, China in 2005. She joined the State Key Laboratory of Tribology at Tsinghua University from 2005. Her current position is associate professor. Her research areas cover nanotribology, nanostructure & nanotechnology of surface and interface, chemical-mechanical planarization and water-based lubrication.